ANION UPTAKE BY OVERBURDEN MATERIAL AT BOULA CHROMITE MINE, ORISSA

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By

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CERTIFICATE

It is certified that the work contained in the thesis entitled "**ANION UPTAKE BY OVERBURDEN MATERIAL AT BOULA CHROMITE MINE, ORISSA**" by **Mr. SK. MD. EQUEENUDDIN** bearing roll no. Y110336 has been carried out under my supervision and this work has not been submitted elsewhere for a degree.

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ABSTRACT

Mafic and ultramafic bed rocks at the Boula-Nuasahi chromite mines, Orissa show a lateritic soil profile typical of tropical weathering. The uppermost horizon contains goethite, FeO.OH as the main hydrated iron oxide mineral. Under natural water pH range, goethite has a positively charged surface. Therefore, the lateritic overburden in chromite mines has a high anion uptake capacity.

This thesis summarizes the results of an experimental study of the parameters controlling adsorption of arsenate and phosphate by Boula laterite. It was concluded that uptake increased with finer grain size, lower concentration level and longer contact time. The effect of solution pH was different for arsenate and phosphate. For example, arsenate adsorption was maximum at an intermediate pH of 7.5 whereas phosphate adsorption steadily decreased with increase in pH. This was explained by inner sphere vs. outer sphere complex formation at the goethite surface.

The anion uptake capacity of Boula laterite is higher than the laterite collected earlier from the Sukinda chromite mine. This is because of higher proportion of crystalline goethite in the Boula material. These results, combined with earlier data on chromate adsorption by Sukinda laterite and phosphate adsorption by Kerala laterite, support the idea that laterite can be used as a low-cost material to remove anionic pollutants from drinking water.

CHAPTER 1
INTRODUCTION AND OBJECTIVES

Laterite is a common product of weathering of a variety of rocks in tropical climate under good drainage conditions (Loughnan, 1969). The name comes from a Latin word "later" meaning bricks. This term was originally used by Buchanan in 1807 to describe a soft regolith material, which is excavated in Kerala to make building bricks. Laterite forms by residual concentration of relatively insoluble oxides of iron and/or aluminium and has a reddish brown to dark red colour. Gidigasu (1976) used the term "lateritic soil" to denote a composite material containing iron oxide and clay minerals. Thus both climate and parent rock materials are important in the formation of laterite and lateritic soils. For example, iron rich rocks of mafic and ultra-mafic variety, including those, which have economic mineral deposits of chromite, commonly have a lateritic overburden. Goethite, which is a major constituent of laterite, has a positively charged surface at natural water pH values. Therefore, laterite soils can effectively adsorb anions like chromate, arsenate and phosphate.

These anions are of great environmental significance. Cr (VI) and As (V) in water are toxic and carcinogenic elements. Dissolved phosphate plays an important role in algal growth and subsequent eutrophication problems. Therefore, an investigation of anion uptake property of laterite has many practical applications. Interesting results were obtained by Praharaj (1998) on chromate adsorption by laterite at Sukinda chromite mine of Orissa. The present work has attempted to extend the scope to arsenate and phosphate using similar overburden material from the Boula-Nuasahi mine which is situated about 70 km NE of Sukinda within a genetically related mafic/ultramafic igneous rock body.

The main objectives of this thesis project can be listed as:

1) To record the various horizons present in the weathering profiles exposed in the Boula quarries.
2) To collect representative samples of rock and soil from each horizon for further laboratory study.
3) To establish the primary and secondary mineralogy by standard methods like microscopy and XRD.

4) To study the effect of the parameters such as concentration, time of contact, grain size and pH of the solution on adsorption of arsenate and phosphate by Boula laterite.
5) To compare the adsorption of these two anions with Sukinda laterite and explain the difference in terms of mineralogy.

CHAPTER 2
PREVIOUS WORK

2.1 GENERAL GEOLOGY OF SUKINDA-NUASAHI-BOULA ULTRAMAFIC BELT

The area under discussion is located at the southern margin of Singhbhum craton within the Precambrian shield area of the eastern India. Some of the richest chromite deposits of the country are located within the Boula-Nuasahi igneous complex in Keonjhar district of Orissa, which is about 70km northeast of the more famous Sukinda ultramafic belt in Jajpur-Dhenkanal district. The chromite ore occur as bands, lenses and pockets in weathered (serpentinized) dunite-peridotite group of rock. These are intrusive into the Precambrian metamorphites such quartzite and quartz mica-schist in the form of a lopolith. Most of the earlier workers (e.g. Sahoo, 1995) emphasize the stratiform nature of the chromite bearing ultramafics.

The Sukinda and the Nuasahi-Boula deposits have similar stratigraphy sequences. It is believed that they have been derived from a single magma source with the Sukinda ultramafic as an earlier intrusive and the Boula-Nuasahi rocks as later derivatives. Its scour/slump structures indicate gravity controlled magmatic layers. In Sukinda, the ultramafics are magnesium rich in contrast to Boula-Nuasahi rocks which have less magnesium in dunite-peridotite, pyroxenite assemblages associated with gabbroic to gabbroic-anorthositic mafic rocks and younger granite, granophyres and dolerite dykes. The geological map of Boula-Nuasahi area is given in figure 2.1.

Halder (1967) reported that the main mineral in chromium bearing ultramafics at Boula-Nuasahi igneous complex is olivine, which is commonly altered to serpentine, talc and pyrophyllite. The peridotite and pyroxenites contain olivine, enstatite and augite where as the gabbroic-anorthosite have in addition to the mafic minerals calcic plagioclase, K-feldspar, quartz, Ti bearing magnetite and ilmenite.

Sahoo (1995) mentioned that the chromite seams at Boula-Nuasahi are thinner (5 to 10m) compared with 10 to 50m thick chromite seams found at Sukinda. The bed rocks at both locations show the development of a thick laterite-limonitic overburden (Table 2.1). The overburden at Sukinda has been reported to be nickeliferous. Sahu and Venkateswaran (1989) observed that Ni was more concentrated in the amorphous hydrated Fe-Oxide phase within the laterite. The origin of nickel is a subject of research

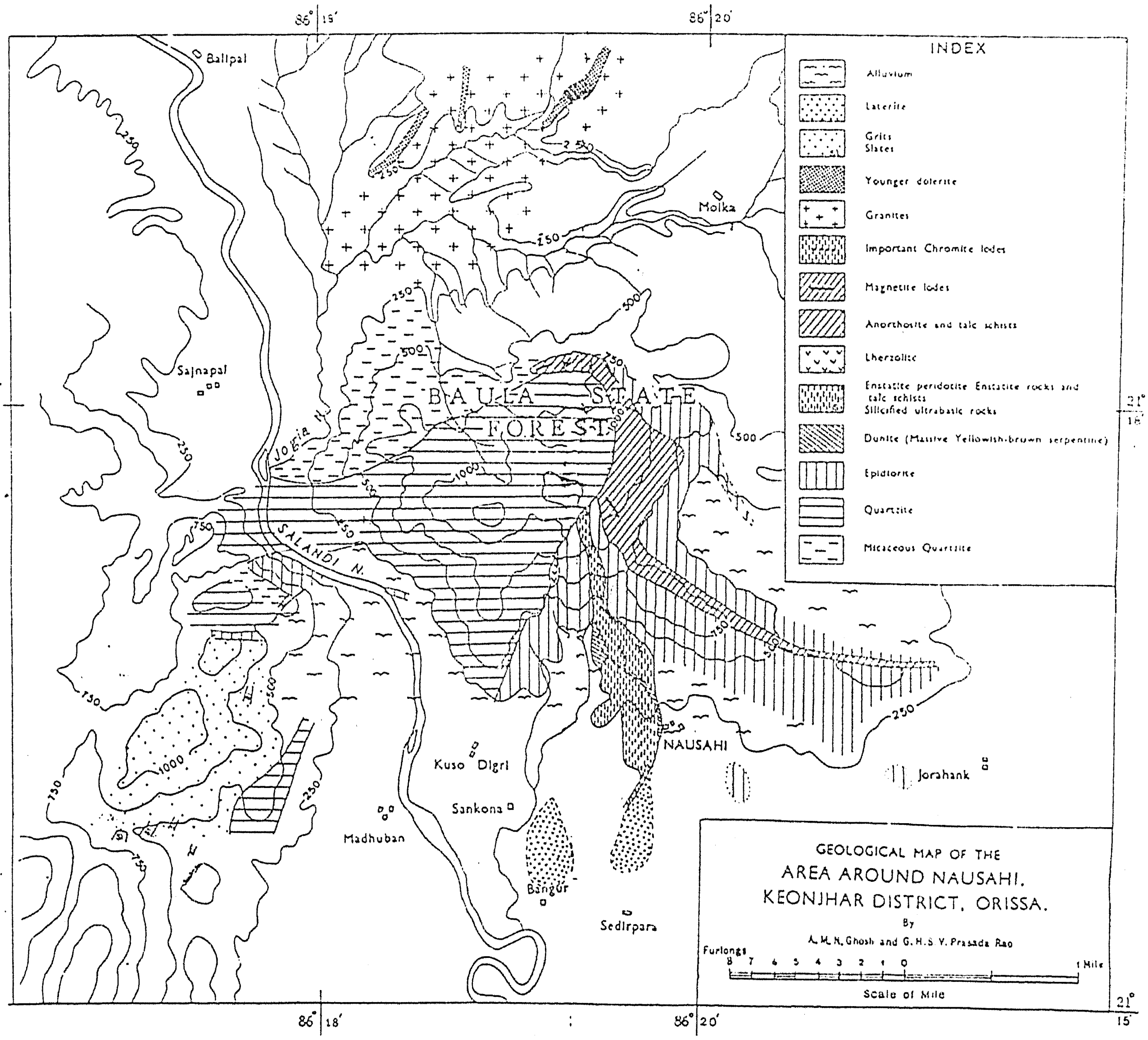

Figure 2.1. Geological Map of Boula-Nuasahi after Ghosh and Rao (1952).

but it is generally believed that it occurs within the mineral structure of goethite which is one of the dominant constituents of the laterite.

2.2 CHROMATE UPTAKE BY LATERITIC SOIL AT SUKINDA

In a recent study Godgul and Sahu (1995) investigated the problem of contamination of ground water by hexavalent chromium in the Sukinda chromite belt. These authors reported high levels of Cr (1000ppb) in the mine floor water. On the other hand, some of the village wells had almost undetectable levels of Cr. This observation was explained by scavenging of hexavalent chromium anion, (CrO_4^{2-}) by goethite in the lateritic matrix.

This work was followed up by laboratory experiments on samples of overburden materials collected from Sukinda by Raymahashay and Praharaj (1998). It was concluded that the formation of iron oxide compounds in the lateritic overburden by oxidation of bed rock is also responsible for Cr (VI) species generated from Cr (III) originally present in chromite ore.

During ground water percolation, the positively charged surface of the hydrated ferric oxides minerals is able to adsorb the chromate (CrO_4^{2-}) anion. Desorption experiments confirmed that presence of crystalline goethite resulted in maximum retention of hexavalent chromium on laterite. On the other hand, the desorption of Cr (VI) was less from the samples containing poorly crystalline goethite and large proportion of maghemite. This result was found to be similar to the adsorption-desorption of phosphate on laterite.

Table 2.1. Stratigraphy of Boula and Sukinda after Sahoo (1995)

		Boula	Sukinda
Recent to Pleistocene		Soil, Alluvium Laterite	Soil, Alluvium Laterite
		- - - - -Unconformity- - - - - - - - -	- - - - - - - Unconformity- - - - - - - - - - -
		Dolerite Dykes Granite Granophyre	Dolerite Granite Gabbro-diorite
Precambrian	Ultramafics	Gabbro-anorthosite With Ti-V magnetite ore bodies Enstatite-peridotite and dunite with chrome ore	Pyroxenite Dunite-Peridotite with Chrome ore
	Metasediments and metavolcanics	Quartzite, quartz-mica schist, quartz-sericite schist	Grity Quartzite Meta-volacanics
		- - - - - Base not seen- - - - - - - - -	- - - - - - - - Base not seen- - - - - - - - - -

2.3 PHOSPHATE UPTAKE BY LATERITIC SOIL AT KERALA

The type area of laterite in India is the Midland region of Kerala, lying between the Highlands to the east and the Coastal Belt to the West. Extensive residual soil profiles have developed over Precambrian charnockite and biotite gneiss throughout this region. The main constituents of lateritic soil are halloysite of intermediate hydration along with kaolinite, gibbsite, goethite and quartz. Experimental work (Raymahashay *et al.*, 1984) showed that this soil can almost completely remove 2 to 50 mg/L dissolved phosphate. The uptake capacity of lateritic soil was higher than pure kaolinitic clay. This was clearly related to the presence of halloysite along with iron hydroxide and kaolinite. As expected for anion uptake, greater amount of phosphate was removed from acidified solution and longer time of contact. Comparison with black cotton soil (Raymahashay *et al.*, 1990) showed that laterite soils have greater phosphate adsorption and retention capacity. For both the soils, adsorption was less in the presence of chloride concentration typical of low salinity part of an estuary.

2.4 ARSENIC REMOVAL BY LATERITE

Arsenic toxicity in ground water of the Ganges delta area has recently attracted world wide attention (Mandal et al., 1996; Acharyya et al., 2000). Several conflicting hypotheses have been put forward to explain the source and occurrence of high levels of dissolved As (III) and As (V) species. The most widely accepted idea is that arsenic was transported as an adsorbed phase on hydrated iron oxides minerals in river sediments (Raymahashay and Khare, 2003). Subsequent reductive dissolution of minerals like goethite occurring in the aquifer has mobilized the adsorbed arsenic back to the ground water (Nickson et al., 1998).

A detailed experiment work has done by Prasad (1994) on removal of As (V) by hematite. He characterized parameters like time, temperature, particle size, and pH for uptake of arsenic on the positive surface of hematite. More recently, the idea of adsorption of arsenic by hydrated ferric oxide has been adopted by Bhattacharya et. al (2001) for use of laterite blocks as a low cost material for removal of arsenic in drinking water. These authors also studied the effect of particle size, time, and initial concentration on the efficiency of arsenic removal.

2.5 MECHANISM OF ANION UPTAKE BY LATERITIC SOIL

As discussed above, one major constituent of laterite soils is Hydrated Ferric Oxide (HFO). In colloidal size fraction, the Fe – OH functional groups at the interface between mineral and water show pH-dependent surface charge (Evans, 1989). For example, at low pH values, a protonation reaction like

$$\equiv Fe - OH + H^+ \longrightarrow [Fe - OH_2]^+$$

gives a positively charged surface. On the other hand, at high pH values, dissociation or de-protonation takes place by reaction such as:

$$\equiv Fe - OH + (OH)^- \longrightarrow [Fe\text{-}O]^- + H_2O$$

Or $$\equiv Fe - OH \longrightarrow [Fe\text{-}O]^- + H^+$$

This gives a negative surface charge at high pH. At an intermediate pH, known as pH for Zero Point of Charge (pH_{ZPC}) net surface charge is zero. Typical values of pH_{ZPC} are 7.3 to 7.8 for goethite, 5 to 9 for hematite, 6.7 for maghemite and 8.5 for amorphous $Fe(OH)_3$ (Krauskopf and Bird, 1995). As a result, for pH value less than pH_{ZPC} the positively charged mineral surface is able to adsorb anions like CrO_4^{2-}, $H_2PO_4^-$, $H_2AsO_4^-$.

The adsorption itself takes place by two principal mechanisms: (1) Inner sphere complex where the anion enters the mineral structure by ligand exchange and (2) Outer sphere complex where the anion is taken up mainly by electrostatic attraction. It is obvious that the overall anion uptake decreases at pH value above pH_{ZPC}. On the other hand, formation of inner sphere complex is independent of pH of the medium (Drever, 1997).

In a typical laterite soil, in addition to HFO, clay minerals and organic matter also contribute to anion uptake but to a limited extent. It is known, for example, that the clay colloids have mostly negative charge except at the particle edges. Therefore, they have much greater cation exchange rather than anion uptake (Raymahashay, 1996).

CHAPTER 3
METHODOLOGY

3.1 SELECTION OF SITE

The study area lies in the Keonjhar district, Orissa. The Boula-Nuasahi-Bangur (BNB) mafic and ultramafic complex is bounded by latitude N21°15'- 21°20' and longitude E86°18'-86°20' and lies in the toposheet no. 73 K/7. The BNB complex occurs in an area of about 5sq.km along N-S from Boula in the north through Nuasahi in the middle and Bangur in the south. The ultramafic body has a maximum width of about 1km in the middle tapering gradually towards north and south. The exposed ultramafic body such as dunite-peridotite, pyroxenite extends in a NNW-SSE direction surrounded by meta-sedimentaries of Iron Ore Group towards northwest and north. The gabbro-anothosite rocks occupy the eastern part of the complex. The area can be approached from Bhadrak via Anandapur. It is about 120km from the state capital Bhubaneswar.

The BNB complex has typical monsoonic climate. The average annual rainfall is around 2498 mm, out of which 1976 mm is precipitated during the southwest monsoon from mid-June to mid-October. The relative humidity varies from 66.12 % to 92.34 %. The maximum and minimum temperatures are reported to be 46°C and 14°C. The topographical expression range between 90m to 400m above MSL (Sahoo, 1995).

3.2 FIELD WORK

Most of the work was done at the Indian Metal and Ferro Alloy Ltd (IMFA) and Orissa Mining Corporation (OMC) quarries in and around Nuasahi-Boula Chromite field, Orissa. The field work was carried out in the month of May and June 2002 for seven days to collect representative samples of weathered rocks and soils right from the bottom parent rock zone to the top laterite zone at the IMFA and OMC quarries. The quarry location has been shown in Figure 3.1. These samples were subsequently analyzed in the laboratory.

3.3 LABORATORY WORK

The samples collected in the field were of two types namely, 1) rock samples that were relatively fresh, hard and tough in order to represent the parent rocks, 2) weathering products which were loose and friable.

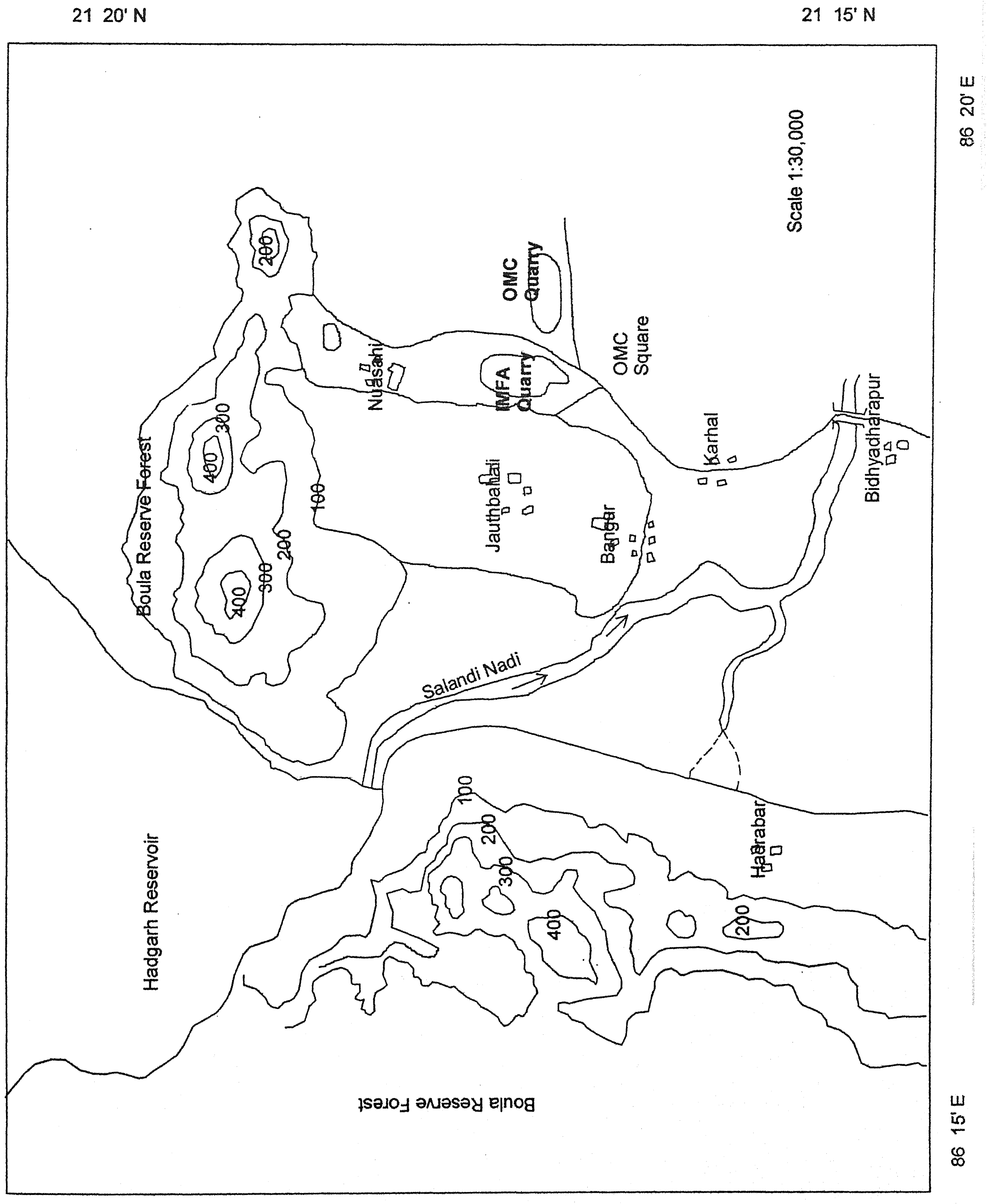

Figure 3.1. Quarry location map at Boula-Nuasahi

3.4 STUDY OF ROCK SAMPLES IN HAND SPECIMEN

Texture, weathering morphology, relative grain size, colour and broad mineralogy were studied in naked eye and under a Bausch and Lomb (USA) binocular microscope.

3.5 STUDY OF ROCKS IN THIN SECTION

Thin sections of selected rock samples were studied under a Leitz Laborlux II petrological microscope.

3.6 X-RAY DIFFRACTION ANALYSIS

To study the detailed mineralogy, rock and soil samples were subjected to X-ray diffraction in bulk powders and oriented slides (prepared by smearing a water suspension on a glass slide). The samples were powered and sieved. The sample passing through ASTM sieve no. 230 (63μ) and retained on ASTM sieve no. 270 (50μ) was used for X-ray diffraction. The samples were scanned under X-ray diffractometer Model ISO Debyeflex 1001 and 2002, Rich-Seifert & Company.

Table 3.1 Working parameters for XRD

X-ray Source	CrKα	CuKα
Scanning speed in 2θ	1.2°/min	1.2°/min
Counts per minute	5K	5K
Time constant	10 sec	10 sec
Current/Volt	30 mA / 40kV	20 mA / 30kV

Relative proportions of minerals were estimated on the basis of the height of XRD peaks. Slow scanning was adopted to resolve doublets and shoulders in the X-ray peaks.

3.7 ADSORPTION EXPERIMENTS FOR ARSENATE AND PHOSPHATE

Standard solution of phosphate and arsenate of 100mg/L was prepared by dissolving 0.143g of diahydrogen orthophosphate, KH_2PO_4 and 0.416g of sodium arsenate, $Na_2HAsO_4.7H_2O$ respectively in 1L of distilled water.

Samples were powered and sieved between 230 to 200 mesh (63μ to 74μ) and 270 to 230 (50μ to 63μ). Phosphate and arsenate uptake by laterite soil was studied by

keeping 1g of soil in contact with 100mL of standard KH_2PO_4 and $Na_2HAsO_4.7H_2O$ solution respectively of requisite concentration and occasional stirring for varying length of time. Then the solution was filtered through Whatman 42 paper and centrifuged. The phosphate remaining in solution after a given contact time was measured by colorimetric stannous chloride method using an acid ammonium molybdate reagent as described below. The concentration of arsenate was measured by using SDDC method.

The pH of the phosphate and arsenate solution was another parameter, which was studied during these experiments. In one set of experiments, initial pH depended on the strength of the KH_2PO_4 and $Na_2HAsO_4.7H_2O$ solution. Such solutions are denoted as "normal solution". On the other hand, parallel experiments were conducted with "acidified solution" in which pH was lowered from average 3.8 to minimum 2.5 for phosphate and from 7.5 to 4.55 for arsenate by addition of 0.1 N HCl drop wise to the normal solution. Similarly, experiments were conducted with "alkaline solution" in which pH was artificially raised from average 3.8 to maximum 10. 5 for phosphate and from 7.5 to 10.18 for arsenate by addition of 0.1N NaOH drop wise to the normal solution.

3.8 STANNOUS CHLORIDE METHOD

This method is used to measure the concentration of phosphate. The principle of this method involves the formation of molybdophosphoric acid, which is reduced to the intensely colored complex, molybdenum blue. This analytical method is extremely sensitive and is reliable down to concentrations below 0.1ppm (mg/L) phosphorus. Analytical procedure given in Standard Methods (1985) was followed. The calibration curve is given in Figure 3.2.

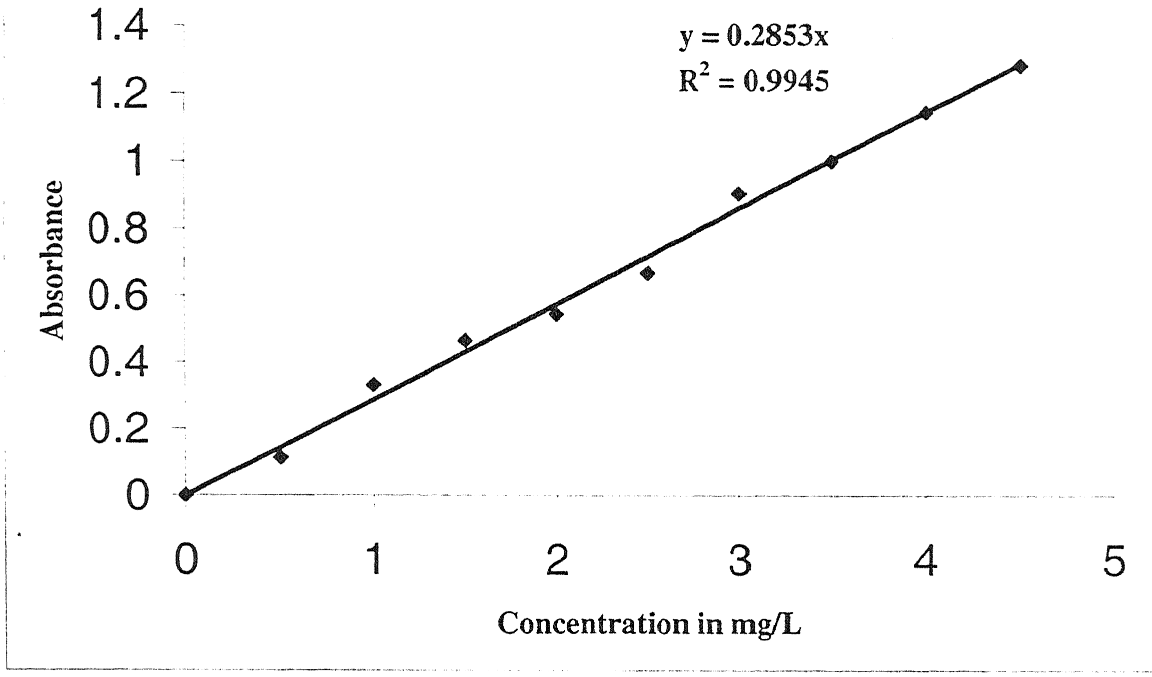

Figure 3.2. Standard curve for measurement of phosphate using Stannous Chloride Method (Wavelength = 690nm, path length = 10mm).

3.9 SDDC METHOD

Total extractable arsenic was analyzed using the Silver Diethyl Dithio Carbamate (SDDC) method as described in the Standard Method (1985). First 35mL of filtered solution were taken in generator. Then rest of steps was followed as mentioned in Standard Method. In this process inorganic arsenic is reduced to arsine (AsH_3) gas by nascent hydrogen generated by the reaction of Zn metal with concentrated HCl. The gas is then passed through a scrubber containing glass wool or cotton impregnated with lead acetate solution into an absorber tube containing SDDC solution (1g SDDC in 100mL pyridine). In the absorber, arsine formed red colored compound by reacting with SDDC suitable for spectrophotometric measurement. The absorbance was measured at 535 nm using a path length of 10mm. The calibration curve was prepared and is given in the Figure 3.3.

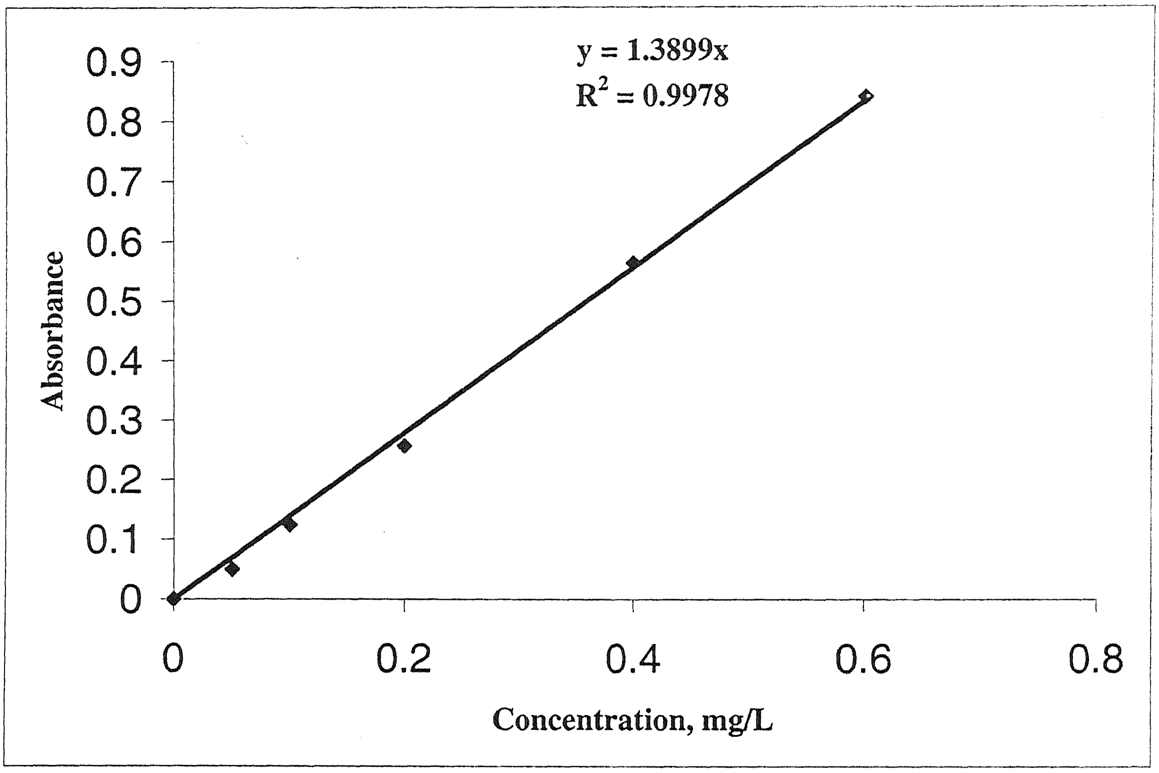

Figure 3.3. Standard curve for measurement of arsenate, As (V) using SDDC method (Wavelength = 535nm, path length = 10mm).

CHAPTER 4

RESULTS AND DISCUSSION

This chapter discusses the results of field work and laboratory study of samples collected from the main quarries in the Boula- Nuasahi chromite mines, Orissa and a comparison with a sample from the Sukinda chromite mines.

4.1 DESCRIPTION OF ROCK AND SOIL SAMPLES

The samples were studied in hand specimen, under binocular microscope, in thin section and by X-ray diffraction (XRD). They have been described below quarry wise according to their location at various levels.

A semi-quantitative estimate of the relative proportion of various minerals (as listed in this chapter) was made from XRD peak height at close 2θ range. The diagnostic peaks selected from Kostov (1968) were 4.2Å (Goethite), 3.10Å (Talc), 3.13 Å (Hornblende), 3.18 Å (Andesine), 3.34 Å (Quartz), 3.33 (Augite), 2.9Å (Maghemite), 3.66 Å (Serpentine), 3.56Å (Kaolinite).

4.1.1 IMFA Quarry:

Twenty samples were collected from the ground level to the lowest bench at the quarry. The quarry extends in N-S direction for a length of about 300m and has maximum width of about 50m. In this quarry, there are two benches. The upper bench is about 8m high and in the next one, about 6m is exposed. The rest being water logged.

i) Sample No. 26/1: 4m below the ground level. Laterite. Dark red in colour. Hard, porous and pisolitic in nature. Highly magnetic in powder. XRD pattern shows the peaks of goethite (4.13 Å) and kaolinite (7.19 and 3.55 Å), which are sharp and of high intensity. A broad and short peak at 2.51 Å can be due to maghemite. The magnetic property is obviously due to maghemite. The relative proportion of various mineral is goethite>kaolinite>maghemite.

ii) Sample No.26/2: 2m below the ground level. Laterite. Dark red in colour. Hard and highly porous in nature. Highly magnetic in powder. XRD pattern shows the predominant sharp peak of goethite (4.15 Å) and broad, high intensity peak of kaolinite (7.17 and 3.58 Å). A short peak at 3.67 Å may be of serpentine but its basal peak at 7.3 Å is missing. A sharp high intensity peak at 2.51 Å can be common to maghemite and goethite. The characteristic peak of quartz at 3.34 Å is also present. The XRD pattern is shown in

Figure 4.1.The relative proportion of various minerals is goethite> kaolinite> serpentine> quartz> maghemite.

iii) Sample No. 26/3: 5m below the ground level. Laterite. Reddish brown in colour. Hard, highly porous and pisolitic in nature. Powder is highly magnetic. XRD pattern shows that goethite is the dominant mineral with sharp peak at 4.16 Å. This sharpness of the peak suggests its crystalline nature. Other mineral constituents are kaolinite (7.23 Å) and maghemite (2.93,2.49 Å).The XRD pattern also shows the major peaks of quartz at 4.32 and 3.33 Å. The mineral proportion is goethite>kaolinite>quartz>maghemite.

iv) Sample No. 26/4: 8m below the ground level. Lateritic rock with ochre. Brown in colour. Very feebly magnetic in powder. Pisolitic in nature. XRD pattern shows a predominant sharp peak of goethite (4.29 Å) and serpentine (7.52, 3.66 Å). The mineral proportion is goethite>serpentine.

v) Sample No. 29/11: 2m below the ground level. Laterite. Dark red in colour. Hard and magnetic in nature. XRD pattern shows the dominant peaks of goethite (4.15 Å) and kaolinite (7.2,3.58 Å). The mineral proportion is goethite>kaolinite.

vi) Sample No. 29/2: 2m below the ground level. Laterite. Dark red in colour. Very hard, high specific gravity. Highly magnetic in powder. XRD pattern shows sharp, high intensity peaks of goethite (4.16 Å) and maghemite (2.95,2.51 Å) with minor peaks of serpentine (7.29,3.7 Å). High magnetic nature is due to the dominance of maghemite. The mineral proportion is goethite>maghemite>serpentine.

vii) Sample No. 26/5: 4m below the ground level. Laterite. Brown in colour. Hard and highly magnetic. The XRD pattern shows sharp peaks of kaolinite (7.20,3.58 Å) and broad peak of goethite (4.14 Å). The minor peaks of chromite are present at 2.89, 2.17 Å and a broad peak at 2.42 Å in combination with kaolinite. A broad peak at 2.50 Å can be due to maghemite. The mineral proportion is goethite>kaolinite>chromite>maghemite.

viii) Sample No. 29/14: 4m below the ground level. Laterite. Dark red in colour. Hard and less magnetic. Pisolitic structure. The major mineral constituents are goethite and serpentine with sharp and high intensity peaks at 4.29,7.56 Å respectively. Short peaks at 4.58 and 2.55 Å may be due to smectite but the diagnostic basal peak at 14 Å is missing. The mineral proportion is goethite>serpentine>smectite (?).

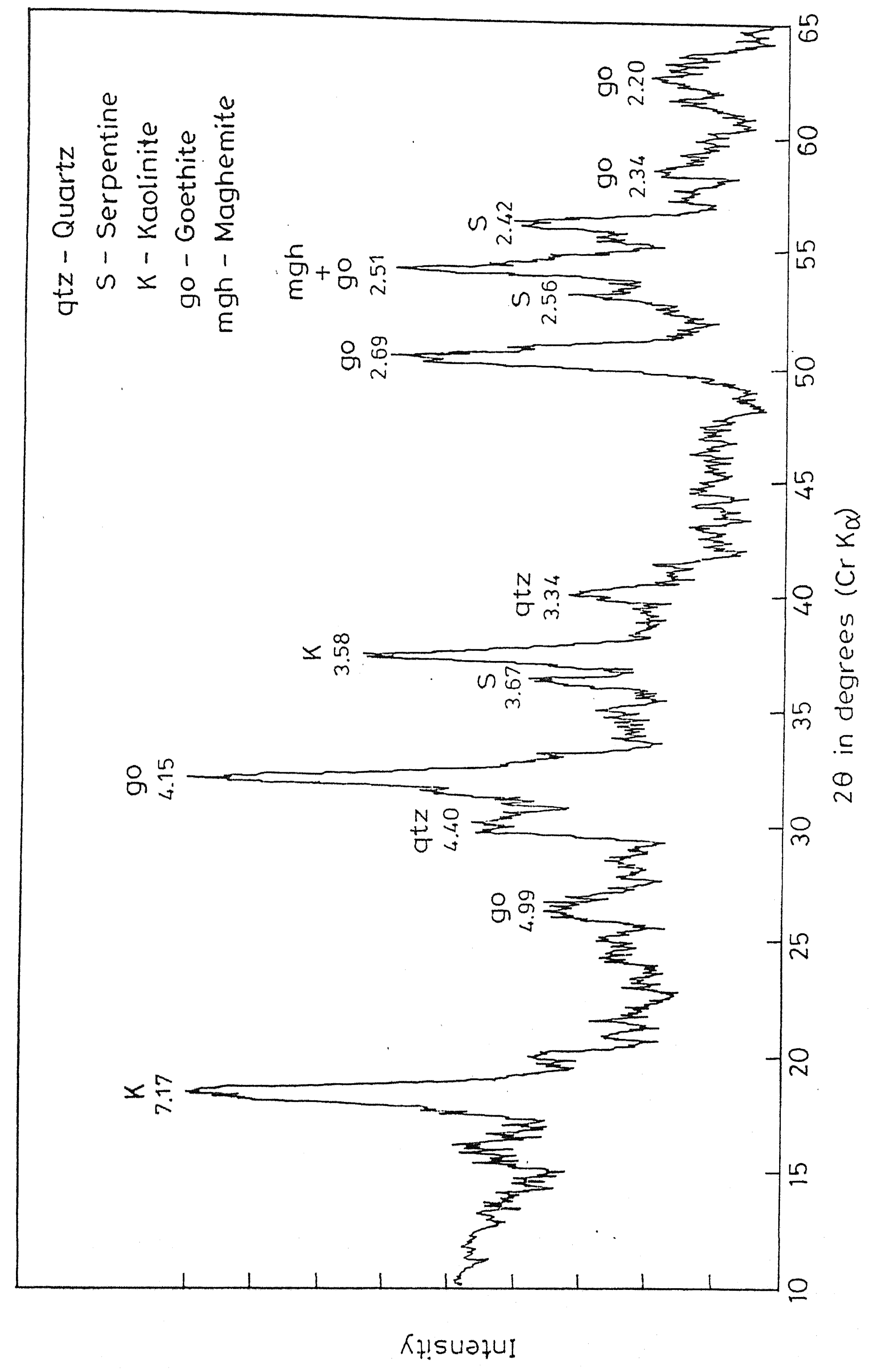

Figure 4.1. XRD pattern of Sample No. 26/2

ix) Sample No.28/2: 12m below the ground level. Limonitic rock. Yellowish brown in colour. Highly magnetic in powder. The major mineral constituents are goethite with sharp peak at 4.17 Å and serpentine (7.28,3.58 Å) and minor maghemite (broad peak at 2.51 Å). The mineral proportion is goethite>serpentine>maghemite.

x) Sample No. 28/1: 8m below the ground level. Limonitic rock. Yellowish brown in colour. Friable and easily powdered on hammering. Magnetic in powder. The XRD pattern shows the sharp, high intensity peak of lepidocrocite (6.74,3.35 Å) with shorter peaks of goethite (4.18 Å). Minor amount of serpentine is present as only very short peak at 7.37 Å is seen in XRD pattern. The proportion of mineral constituents is lepidocrocite>goethite>serpentine.

xi) Sample No. 29/9: 10m below the ground level. Limonitic rock. Yellowish brown in colour. Highly magnetic in powder. The XRD pattern shows the dominant sharp peak of goethite (4.18 Å) and short peaks of talc (9.43, 3.12 Å), serpentine (7.34 Å) and smectite (?) at 4.51, 2.56 Å. The mineral proportion is goethite> talc> serpentine> smectite (?).

xii) Sample No. 29/10: 13m below the ground level. Soft limonitic rock. Greenish yellow in colour. Magnetic in powder. The main XRD peaks are talc (9.31,3.10 Å), goethite (4.15 Å), smectite (?) at 4.45 and 2.58 Å. The mineral proportion is goethite>smectite (?) > talc.

xiii) Sample No. 29/1: 5m below the ground level. Partly altered parent rock. Greenish in colour Soft, friable and non-magnetic in nature. The XRD pattern shows the sharp peaks of talc(9.28, 3.10 Å) and a broad peak of smectite (?) at 4.49, 2.54 Å. The mineral proportion is talc>smectite (?).

xiv) Sample No. 29/3: 6m below the ground level. Partly altered serpentinite. Brownish white in colour with greenish tint at some portion. Soft, scratched by nail. Non-magnetic in powder. The XRD pattern shows the dominance of talc by sharp, high intensity peaks at 9.31,3.12 Å and a very short peak of smectite (?) at 4.55 Å. The mineral proportion is serpentine>quartz>talc>smectite (?).

xv) Sample No. 28/5: 12m below the ground level. Partly altered parent rock. Brownish yellow in colour. Soapy feeling and scratched by nail. Non-magnetic in powder. The main XRD peaks are of serpentine (7.57, 3.66 Å) and short peaks of quartz (4.29,3.42 Å)

and smectite(?) at 4.5, 26 Å. The mineral proportion is serpentine>smectite(?)>quartz.

xvi) Sample No.30/4: Relatively fresh parent rock. Whitish green in colour. Non-magnetic in powder. This sample was collected at depth of about 10m below the ground level.The XRD pattern shows the dominant peaks of plagioclase feldspar of andesine composition (6.29,3.16 Å) and talc (9.32, 3.10 Å). The mineral proportion is andesine>talc.

xvii) Sample No.28/11: 12m below the ground level. Relatively fresh parent rock. Dark brown in colour. Hard, high specific gravity and highly magnetic in powder. The XRD pattern shows the major peaks of hornblende (8.05,4.96, 3.34, 3.09, 2.69 Å), and short minor peaks of chromite (2.82, 2.45 Å) and augite (3.09, 3.0 Å). The high specific gravity is mainly due to the presence of chromite. The mineral proportion is hornblende>augite>chromite.

xviii) Sample No. 28/10: 15m below the ground level. Relatively fresh parent rock. Greyish green in colour. Hard and magnetic in powder. The XRD pattern shows the major sharp, high intensity peaks of augite (3.31,2.49 Å) and talc (9.35, 3.115 Å). A peak of quartz is also present at 4.25 Å. High intensity peak at 3.31 Å may be due to combined reflection of quartz and augite. Short peaks at 2.49, 2.22 Å may be identified as olivine. The XRD pattern is shown in Figure 4.2.The mineral proportion is talc> quartz> augite> olivine.

4.1.2 OMC Quarry:

OMC quarry is located on the East of IMFA quarry. Six samples were collected from the ground level to the depth of about 5 to 6m, which is first bench. One sample numbered 31/5 was collected from dump site created from underground mining.

i) Sample No. 31/2: 1m below the ground level. Laterite. Dark red in colour. Hard and only few grains are magnetic in powder. The XRD pattern shows the sharp peaks of goethite (4.15 Å), short peaks of kaolinite (7.18, 3.56 Å), serpentine (7.38, 3.59 Å), quartz(4.24,3.35 Å). The mineral proportion is goethite>kaolinite>serpentine>quartz.

ii) Sample No. 31/7: 2m below the ground level. Laterite. Dark red in colour. Hard, highly magnetic. The XRD pattern shows the dominant of peak of goethite (4.13 Å), which is sharp, and of high intensity along with maghemite (2.93, 2.50 Å), serpentine

(7.28,3.56 Å), lepidocrocite (6.23,2.46,3.32 Å). Maghemite and lepidocrocite at 2.50 and 2.46 Å giving high intensity peak due to combined reflection with goethite. A very short peak occurs at 4.80 Å that may be of gibbsite. The mineral proportion is goethite>serpentine>maghemite>gibbsite (?)>lepidocrocite.

iii) Sample No. 31/6: 5m below the ground level. Greyish white in colour with yellowish tint. Limonitic rock with ochre. Soft, soapy feeling. Magnetic in powder. The XRD pattern shows the sharp, high intensity peak of talc (9.24,3.07 Å), smectite (?) at 4.51, 2.56 Å and maghemite (2.90 Å). The mineral proportion is talc>smectite (?)>maghemite.

iv) Sample No. 31/11: 4m below the ground level. Relatively fresh rock. Greyish white in colour with dark spot at some portion. Hard, non-magnetic. The XRD pattern shows the dominance of andesine (6.35,3.18 Å) and minor quartz (short peak only at 4.24 Å). Minor amount of talc is also present shown by the occurrence of one peak at 9.41 Å. The mineral proportion is andesine>talc>quartz.

(v) Sample No. 31/4: 4 m. below the ground level . Relatively fresh rock. Hard, vitreous luster, very feebly magnetic. Greyish white in colour. The major peaks in the XRD pattern are andesine (6.47,4.01,3.18 Å) and hornblende (8.48,4.92,3.33 Å). The mineral proportion is andesine > hornblende.

(vi) Sample No. 31/5: This relatively fresh sample was collected from the dump site. Greenish black in colour. Hard, vitreous luster and feebly magnetic. Thin section shows pyroxene (colourless, non-pleochroic, high relief, two sets of nearly right angle cleavage, third order interference colour), hornblende (pleochroic from pale green to yellow, two set of oblique cleavage, high relief) and plagioclase (grey colour, lamellar twinning, low relief). The extinction angle of plagioclase was measured around 23°. Therefore, from Michel-Levy chart (Kerr, 1961) the composition of plagioclase is identified to be andesine. The presence of hornblende and andesine was also confirmed by the XRD pattern, which shows the dominant peak of hornblende (9.07,4.53,3.13,2.72 Å) and andesine (6.30,3.18 Å). The XRD pattern is shown in Figure 4.3. The mineral proportion is hornblende > andesine.

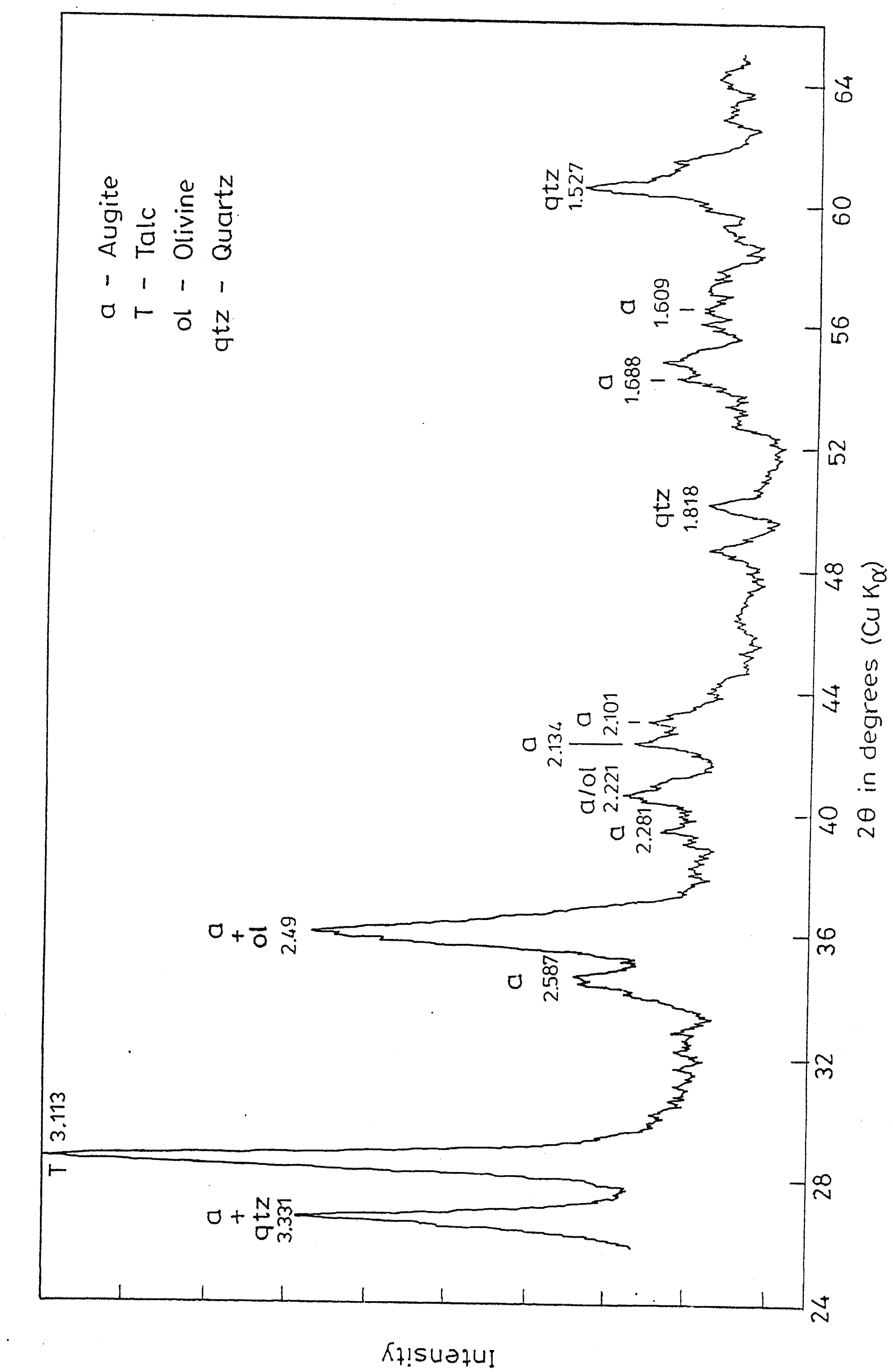

Figure 4.2. XRD pattern of Sample No. 28/10

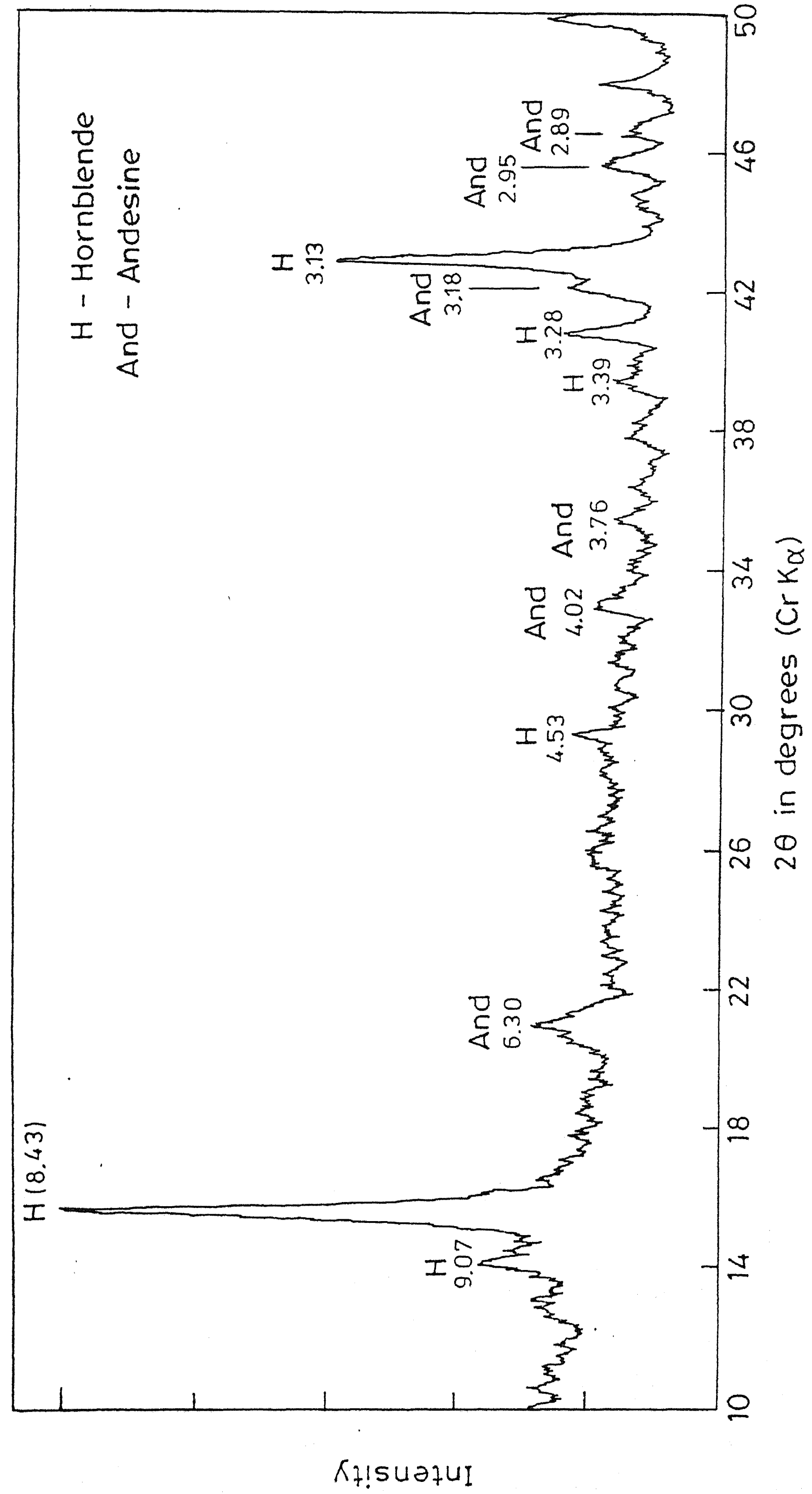

Figure 4.3. XRD pattern of Sample No. 31/5

4.1.3 Sukinda Sample

For comparison of anion uptake capacity with Sukinda overburden material, one sample was selected from the collection by Praharaj (1998). This sample has the following description.

Weathered chromiferous limonite. About 42m below the ground level. Relatively soft. Reddish brown in colour. White aggregates of serpentine seen under binocular microscope. Highly magnetic in powder. XRD pattern shows that goethite (4.18 Å) is the dominant mineral, which is accompanied by maghemite (2.50 and 2.93 Å) and minor serpentine (3.63 Å). A sharp and high intensity peak at 2.43 Å can be common to chromite and goethite.

4.2 WEATHERING PROFILE

From the mineralogy of the samples as described above and their relative positions in various quarries, a generalized vertical profile according to the stages of weathering can be worked out, presented in Table 4.1. From the mineralogical composition of the relatively fresh and partly altered rocks, it can be concluded that the parent rocks are gabbroic-anorthosite and pyroxenite. However, the fresh rocks are rarely exposed in the quarries due to water logging. Alteration is relatively less intense in OMC quarry in comparison to IMFA quarry.

Zone-4 is the bed rock due to its fresh appearance and the presence of minor olivine, augite, the primary minerals. This zone is also dominated by hornblende, serpentine, talc and andesine. A minor quantity of chromite is also present in one sample i.e. Sample number 28/11. From thin section study it was concluded that the augite was altered to hornblende due to the presence of irregular contact between these two minerals and in upper layers, all the hornblende, pyroxene and olivine present in zone 4 have been converted to talc and serpentine. As we move from the zone 4 to zone 3, there is a distinct change in mineralogy, nature and colour of the rock samples. The dominant minerals are talc, serpentine and probably smectite. However, zone 2 i.e. mottled zone shows a marked contrast in mineralogy. It shows the development of iron oxyhydroxides and the rock is highly weathered, soft, friable, yellowish or greenish brown in colour. The dominant mineral in this zone is goethite (FeO.OH) followed by talc, serpentine, smectite

and maghemite. But in sample no. 28/1, lepidocrocite (FeO.OH, polymorph of goethite) is the dominant mineral. Maghemite (v- Fe_2O_3) is probably a product of dehydration of lepidocrocite. The presence of Fe – mineral is due to the accumulation of insoluble residues of low temperature weathering. This has probably been brought about by the prolonged exposure of parent rocks to atmospheric oxygen and percolating ground water. As we move from the mottled zone to zone 1 i.e. laterite(ferricrete) zone, there is a distinct change in colour and rock type. This zone consists of hard, dark red to reddish brown laterite with dominance of goethite as in zone 2 but kaolinite, which is probably a product weathering of smectite is also present in higher proportion than serpentine. Minor smectite and chromite are present in some samples.This zone is the final oxidized and weathered product of the bed rocks.

In summary, the weathering profile in IMFA quarry shows the following features:

1. Occurrence of talc, andesine, serpentine, augite, hornblende,olivine and minor chromite in the bed rock at about 12m below the ground level.
2. Development of smectite in the zone 3 along with talc and serpentine.
3. Dominance of goethite in the zone 1 and zone 2.
4. Decrease of serpentine and increase of kaolinite in the topmost zone 1.

The weathering profile in OMC quarry is more or less the same as IMFA quarry, but weathering is less intense. For example, sample 31/11, 31/4 in OMC quarry collected below a depth of about 5m and sample no. 31/5 from the underground excavation are relatively fresh and contain X-ray peaks of hornblende and andesine. This represents the bed rock zone (zone 4 at IMFA quarry). The other sample 31/6, greyish white in colour from a depth of about 5m shows X-ray peaks of talc, maghemite along with the development of smectite, which might represent the transitional clay zone in between the bed rock and limonite (zone 3 at IMFA quarry). The other samples 31/2, 31/7 collected between 1-2m below the ground level show X-ray peaks of goethite followed by kaolinite, serpentine, maghemite, gibbsite with minor lepidocrocite. But goethite is the dominant mineral. So these two samples may represent the ferricrete zone. Plate 4.1 and 4.2 show typical laterite profiles in this area.

Table4.1. A generalized vertical weathering profile in IMFA quarry

Zone	Description	Corresponding Samples	Mineral Proportions
1 Laterite (Ferricrete) Zone 2 to 8m below Ground Level (GL)	Dark red, reddish brown in colour, hard and often pisolitic	26/1, 26/2, 26/3, 26/4, 29/11, 29/2, 26/5, 29/14	Go>Ka>Ser>Qtz>Mgh ± Chr ± Sm
2 Mottled Zone 8 to 13m below GL	Soft, limonitic, yellowish brown and greenish yellow in colour	28/2, 28/1, 29/9, 29/10	Go>Talc>Ser>Sm>Mgh ± Lep
3 Pallid Zone 6 to 12m below GL	Greenish and brownish white in clour, soft, partly altered rock	29/1, 29/3, 29/13, 28/5	Ser > Qtz > Talc> Sm (?)
4 Fresh Rock more than 8 - 12m from GL	Greyish white, Greyish green, dark brown in colour. Pyroxenites, Gabbroic-Anorthosite	28/10 28/11 30/4	Talc>Qtz>Augite>Ol Hb>Augite>Chr And>Talc
Go – Goethite, Ka – Kaolinite, Ser – Serpentine, Qtz – Quartz, Lep – Lepidocrocite, Mgh – Maghemite, Chr – Chromite, Sm – Smectite, Hb - Hornblende, And – Andesine, Ol-Olivine			

Plate 4.1. The development of lateritic overburden at IMFA quarry.

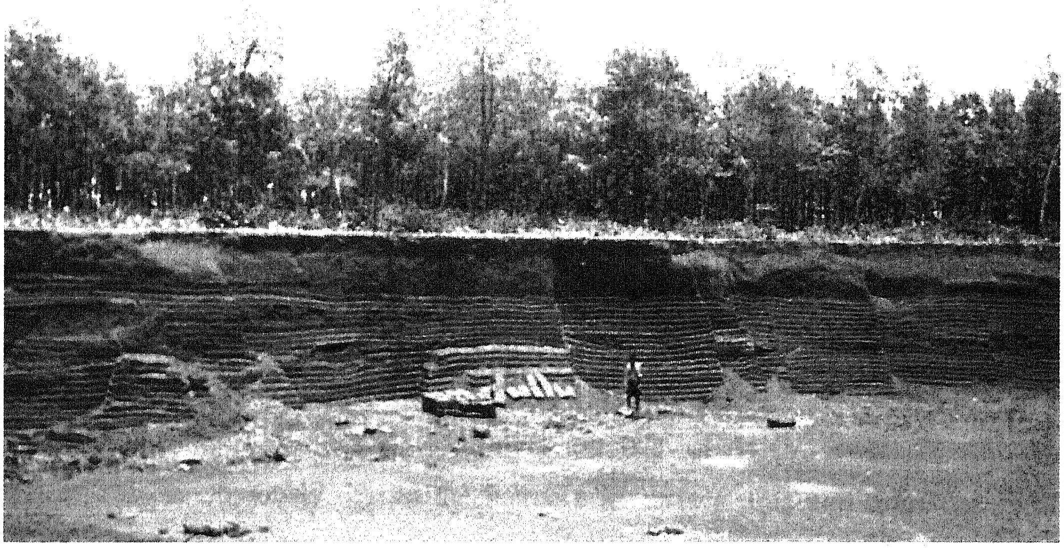

Plate 4.2. Laterite quarry near Bangur village.

4.3 ANION UPTAKE

Batch experiments were designed to study the uptake of arsenate and phosphate anion by the lateritic overburden materials collected from the Boula chromite mine. This was compared with the uptake by the selected sample of Sukinda laterite. Details of the experimental procedure have been given in chapter 3.

4.3.1 Removal of As (V)

Dissolved arsenic occurs as arsenite, As (III) and arsenate, As (V) species. In the pH range of 3 to 11, the higher valency As (V) occurs as the oxy-anions $H_2AsO_4^{1-}$ and $HAsO_4^{2-}$ (Drever, 1997). Their relative concentration is controlled by pH through the equation

$$H_2AsO_4^{1-} = HAsO_4^{2-} + H^+$$

Dissociation Constant K= $10^{-6.97}$ at 25°C.

Therefore, at pH below 6.97, the concentration of $H_2AsO_4^{1-}$ is higher than $HAsO_4^{2-}$ and at pH above this, the concentration of $HAsO_4^{2-}$ is higher than $H_2AsO_4^{1-}$.

As discussed earlier, the adsorption of arsenate anion on the positively charged surface of hydrated iron oxide (goethite) is controlled by several simultaneous processes. These are

1) Relative abundance of $H_2AsO_4^{1-}$ and $HAsO_4^{2-}$ as controlled by the solution pH.
2) The pH dependent surface charge of hydrated iron oxide. The pH_{ZPC} being 6-9 (7.3 to 7.8 for goethite), the surface is positively charged below and negative above this value.
3) Formation of inner sphere and outer sphere complexes. Outer sphere complexing, also called non-specific adsorption, is based on electrostatic attraction and is, therefore, pH dependent while formation of inner sphere complex (specific adsorption) is independent of pH.

In the present experiments, the removal of As (V) by Boula and Sukinda laterite has been studied by changing various parameters such as grain size, time, pH, and concentration. The results have been discussed below.

Table 4.2 shows that for all As_i values, removal of As (V) increases with finer grain size. This is obviously due to the increase in surface area and therefore greater adsorption. The removal also decreases with increase in initial As_i concentration because

the adsorption sites become saturated at high concentration levels. The same data have been plotted in Figure 4.4.

Table 4.2. Effect of Grain Size and As (V) concentration for fixed contact time =24 hrs at room temperature ≈ 20°C and 1% suspension. As_i and As_f denotes initial and final As (V) concentration.

Sample	Grain Size	As_i mg/L	As_f mg/L	% Removal
Boula Laterite	63μ to 74μ	0.5	0.0259	94.82
		2.0	0.214	89.3
		4.0	0.81	79.75
		8.0	3.65	54.37
Boula Laterite	50μ to 63μ	0.5	0.0	100
		2.0	0.159	92
		4.0	0.356	91.1
		8.0	1.02	87.25

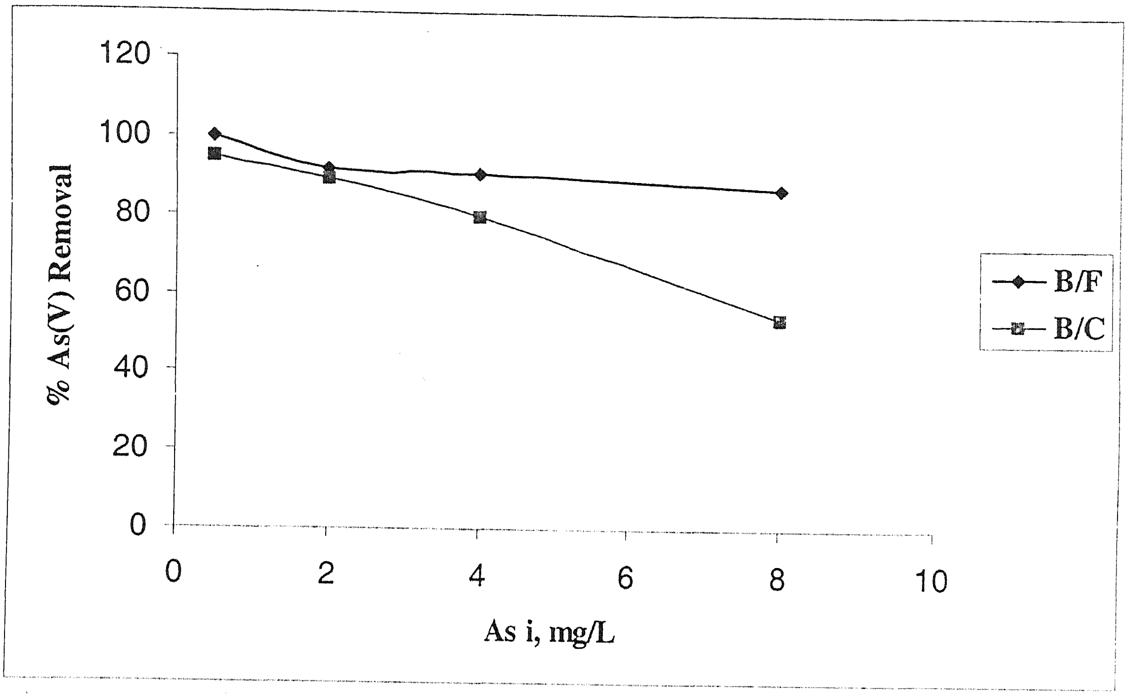

Figure 4.4. Effect of grain size and concentration on removal of As (V). B/C and B/F represent the coarse and fine fraction of Boula Laterite.

Table 4.3 shows that the percentage of removal is more when contact time is more. The same data plotted in Figure 4.5 showed that removal is faster in the beginning. This is because larger number of the positively charged sites are exposed to the anions and also the more OH^{1-} from the iron hydroxide surface are replaced by As (V) ion to form inner sphere complex. The sites become saturated after longer time.

Table 4.3. Effect of Contact Time with coarse fraction of Boula Laterite.

As_i =8mg/L, 1% suspension, at room temperature ≈ 20°C.

Sample	Grain Size	Time in hrs	As_f mg/L	% Removal
Boula Laterite	63μ to 74μ	24	3.65	54.37
		72	1.18	85.25
		96	0.97	87.88

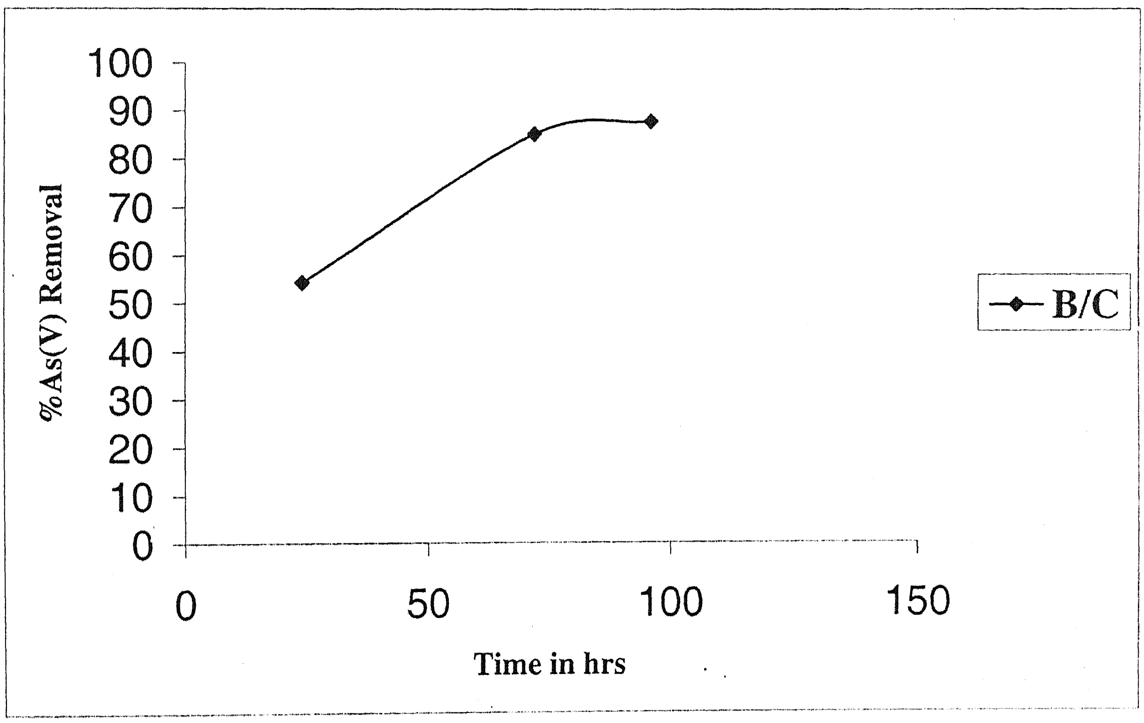

Figure 4.5. Effect of contact time on removal of As (V) by coarse fraction of Boula Laterite

The data given in Table 4.4 and Figure 4.6 shows that the effect of pH on removal of As (V) is a complex process. With increase in pH, the removal increases and then becomes maximum at pH value around 7.5, then decreases to a minimum. This is attributed to more than one reason. As pH increases the surface of the hydrated iron oxides becomes more negative. So there is repulsion between the negatively charged surface and anions such as $H_2AsO_4^{1-}$ and $HAsO_4^{2-}$. At initial pH of 4.55, the $H_2AsO_4^{1-}$ anion is dominant and it forms inner and outer sphere complexes. But with increase in pH, the amount of $H_2AsO_4^{1-}$ will decrease in comparison to $HAsO_4^{2-}$. As pH $_{ZPC}$ is approached, the surface charge is zero. At that time, there is formation of inner sphere complex by ligand exchange only. With further increase in pH, due to development of negative charge on the surface, there is no anion close to the hydrated iron oxides surface to form inner or outer sphere complex. These results are similar to those obtained by Prasad (1994) where As(V) uptake by hematite had a maximum around pH 5.

Table 4.4. Effect of grain size and pH for fixed As_i = 4 mg/L, Reaction time =24 hrs, 1% suspension at room temperature ≈ 20°C.

Sample	Grain Size	pH	As_f mg/L	% Removal
Boula Laterite	63μ to 74μ	4.55[b]	1.32	67
		7.5[a]	0.81	79.75
		10.18[c]	1.33	66
Boula Laterite	50μ to 63μ	4.55[b]	0.777	80.57
		7.5[a]	0.284	92.9
		10.18[c]	0.84	79

a = Normal Solution, b = Acidified Solution, c = Alkaline Solution

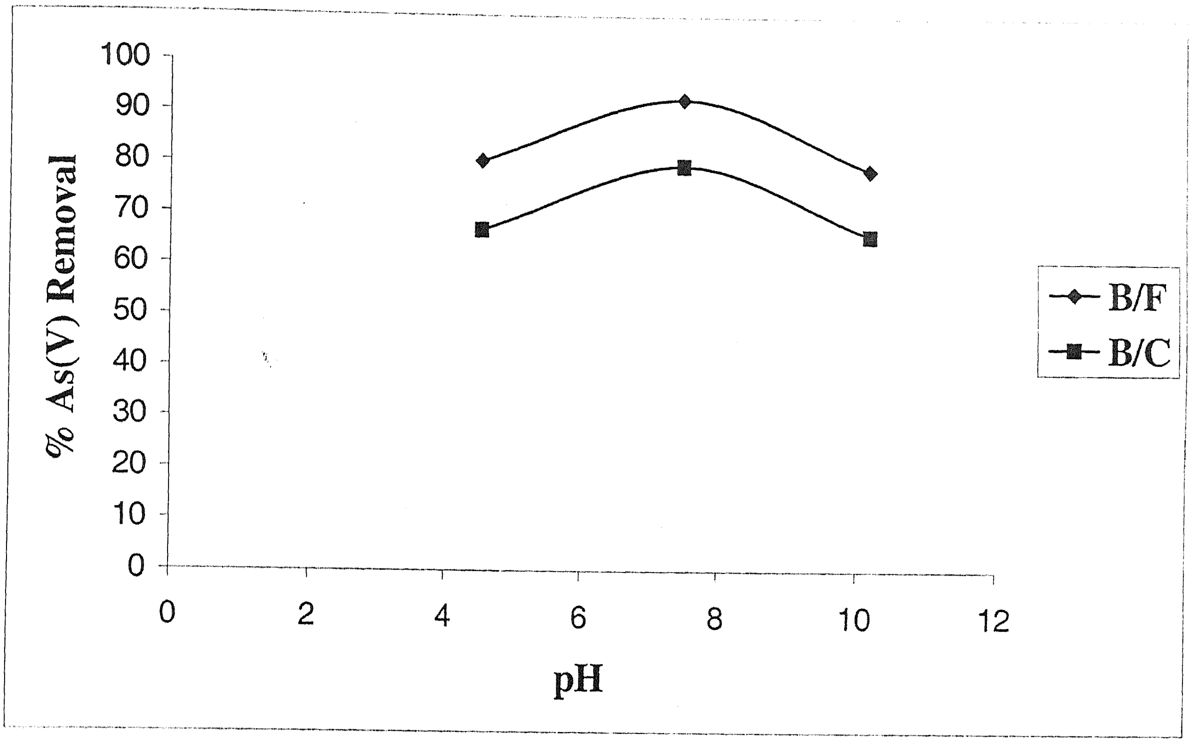

Figure 4.6. Effect of pH and grain size on removal of As (V). B/C and B/F are coarse and fine fraction of Boula laterite.

Table 4.5. Comparison of As (V) removal by Boula and Sukinda Laterite at different As_i values for fixed contact time = 24 hrs and grain size 63μ to 74μ. 1% suspension at room temperature ≈ 20°C.

As_i in mg/L	% Removal by Baula Laterite	% Removal by Sukinda Laterite
0.5	94.82	92.8
2.0	89.30	84.0
4.0	79.75	73.75
8.0	54.37	33.87

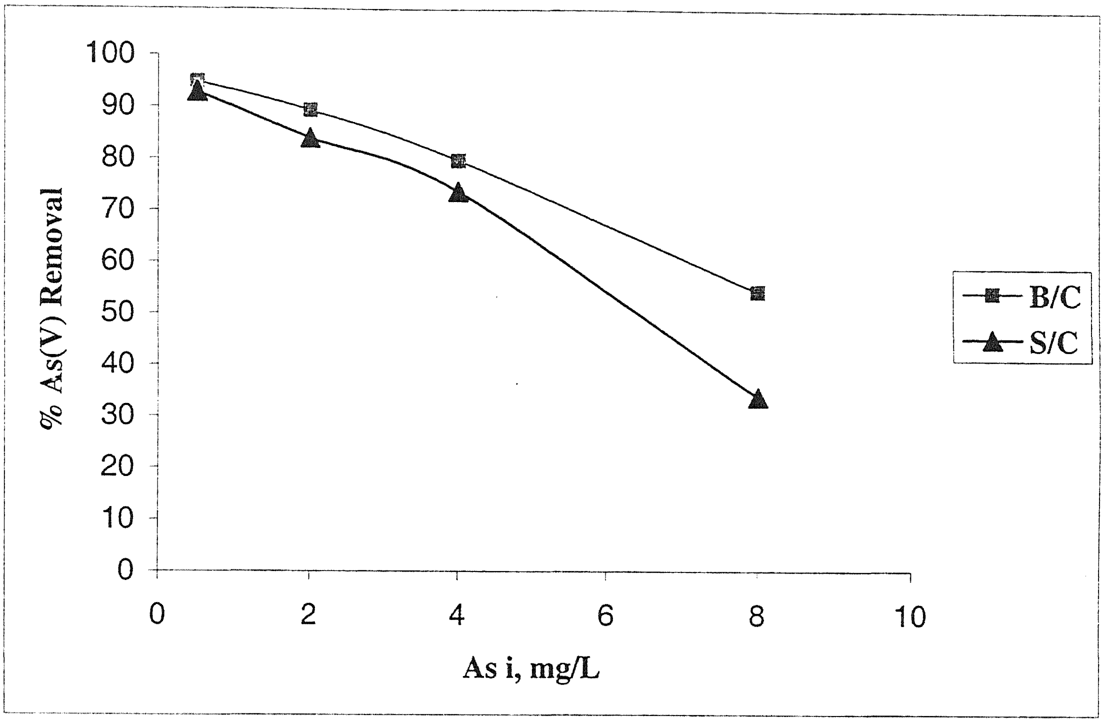

Figure 4.7. Comparison of As (V) removal by Boula and Sukinda Laterite. B/C and S/C are coarse fractions of the two laterites.

4.3.2 Comparison of As (V) Removal with Sukinda Laterite

This comparison is given in Table 4.5 and Figure 4.7. We can conclude that the removal by Baula laterite is more than the Sukinda laterite. This difference between the two laterite samples is caused by the difference in the proportion of goethite and its crystalline nature found from the XRD patterns described below:

i) XRD peak at 4.16Å for goethite and 3.35 Å for quartz was selected because they are in a narrow 2θ range. The peak area ratio of goethite to quartz was found to be 2.84 for Boula laterite and 2.72 for Sukinda laterite shown in Figure 4.8. This suggests that Boula sample has relatively higher proportion of goethite.

ii) The shape of the goethite peak in Baula laterite is also sharper as shown in Figure 4.8. This suggests that mineral is more crystalline in this material. This sharpness can be quantified in a manner similar to the commonly adopted method for clay minerals. For example, the peak width at half height is 0.4 units for Boula and 0.7 for Sukinda. Similarly, peak height: half width (H/W) was calculated to be 26.25 for Boula sample and 15.28 for Sukinda sample. Higher H/W ratio indicates greater crystallinity. Therefore,

Sukinda sample. Higher H/W ratio indicates greater crystallinity. Therefore, higher proportion of more crystalline goethite in Boula appears to be responsible for its higher arsenate adsorption.

4.3.3 Removal of Phosphate

The main dissolved phosphate species between pH 2 and 12 are $H_2PO_4^{1-}$ and HPO_4^{2}. Their relative concentration is controlled by pH through this equation:

$$H_2PO_4^{1-} \quad = HPO_4^{2-} + H^+$$

Dissociation Constant K= $10^{-7.2}$ at 25°C

Therefore, at pH below 7.2, the concentration of $H_2PO_4^{1-}$ is higher than HPO_4^{2-} and at pH above 7.2, the concentration of HPO_4^{2-} is higher than $H_2PO_4^{1-}$.

As discussed earlier for arsenate, the adsorption of phosphate anion on the positively charged surface of hydrated iron hydroxide (goethite) is controlled by

(i) Relative abundance of $H_2PO_4^{1-}$ and HPO_4^{2-}, (ii) pH_{ZPC} of hydrated Fe oxide minerals and (iii) formation of outer and inner sphere complex.

The removal of phosphate has been studied by changing the various parameters such as grain size and pH. The results have been shown in Table 4.6 and Figure 4.9.

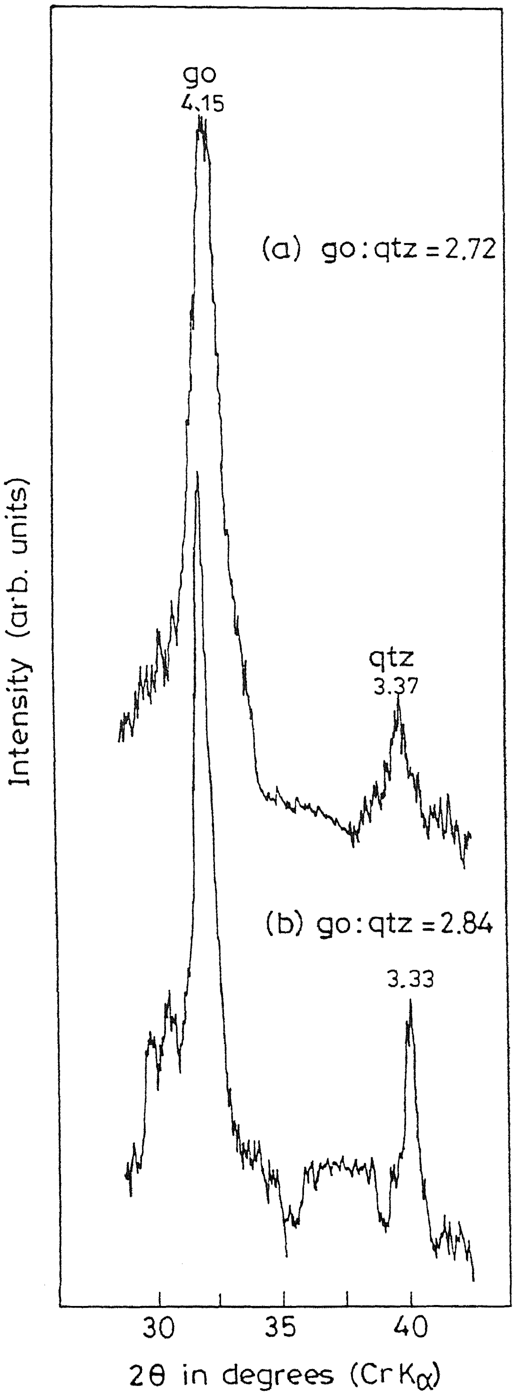

Figure 4.8. Comparison between Boula Lateite Sample No 26/3 and Sukinda laterite.

Table 4.6. Effect of pH and grain size for fixed P_i = 15 mg/L, Reaction time =24 hrs, 1% suspension at room temperature ≈ 20°C. P_i and P_f denotes the initial and final phosphate concentration.

Sample	Grain Size	pH	P_f mg/L	% Removal
Boula Laterite	63μ to 74μ	2.5[b]	4.51	69.9
		3.8[a]	7.09	52.73
		7.4[c]	7.75	48.3
		10.8[d]	11.9	20.6
Boula Laterite	50μ to 63μ	2.5[b]	3.31	77.9
		3.8[a]	4.38	70.8
		7.4[c]	6.27	58.2
Sukinda Laterite	63μ to 74μ	2.5[b]	4.94	67.06
		3.8[a]	7.21	51.9
		7.4[c]	8.48	43.4

a = Normal Solution, b = Acidified Solution, c & d = Alkaline Solution

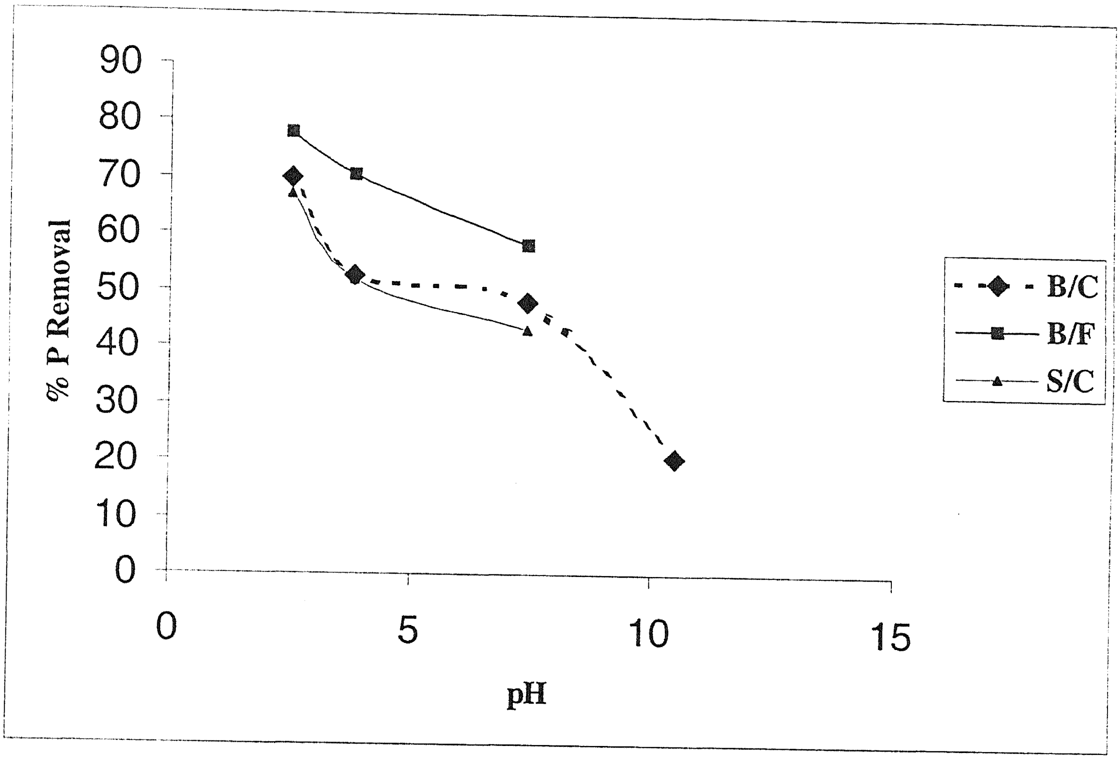

Figure 4.9. Effect of pH and grain size on phosphate removal.

Removal of phosphate by Boula and Sukinda laterite is similar to removal of arsenate by the same material. The percentage of phosphate removal increases with decrease in grain size at a given pH. On the other hand, removal of the phosphate anion decreases as pH increases. The major difference is that there is no peak at an intermediate pH as observed for arsenate although there is a change in slope for the coarse fraction. This may be due to the fact that phosphate is removed only by exchange with OH^- and formation of inner sphere complex.

Once again, the Boula sample removes slightly more phosphate than the Sukinda sample. The difference is less in acidic pH values. This can be explained by greater proportion of crystalline goethite in the Boula material.

CHAPTER 5
SUMMARY AND CONCLUSIONS

From the results obtained during field and laboratory study of the overburden material at Boula-Nuasahi chromite mines, Orissa, the following conclusions can be drawn.

5.1 CONCLUSIONS

1) The weathering profile at Boula-Nuasahi shows typical horizons of residual soil development in tropical climate. Here pyroxenite and gabbroic-anorthosite form the local bed rocks. They are overlain by three weathered layers, which have irregular boundaries among themselves. These are (i) partly altered parent rock, (ii) mottled clay and (iii) laterite. This is similar to the weathered profile at Sukinda (Praharaj, 1998).
2) The major hydrated iron oxide mineral in the overburden material is goethite. It is associated with lepidocrocite and its dehydrated product, maghemite.
3) The positively charged surface of goethite is mainly responsible for uptake of anions like arsenate and phosphate.
4) Removal of arsenate increases with finer grain size of laterite, longer contact time and with lower initial As (V) concentration. Similarly, phosphate removal increases with finer grained laterite in contact for long time.
5) The effect of pH on removal of arsenate and phosphate is different. For arsenate, removal first increases with increase in pH and reaches a maximum at 7.5 and then decreases with further increase in pH. On the other hand, removal of phosphate decreases with increase in pH without reaching a maximum. This difference is apparently due to the relative role of outer sphere vs inner sphere complex formation.
6) Sukinda laterite has a lower anion uptake capacity than Boula laterite because the proportion of crystalline goethite is less.
7) The suggestion of Bhattacharyya et al (2001), that laterite locally available in West Bengal, can be used as low cost material for arsenic removal, is applicable to Boula and Sukinda laterites.

8) Taking the maximum (100%) removal of 0.5 mg/L As (V) by finer grained Boula laterite (Table 4.2); the efficiency of arsenate uptake was calculated to be 50 mg/kg/day.

5.2. SUGGESTION FOR FURTHER WORK

1) These experiments were performed with 1% soil suspension (1 g soil in 100 mL solution) as mentioned in chapter 3. The effect of different soil: solution ratios can be studied as a parameter.
2) Anion uptake data can be further quantified through Adsorption Isotherms and kinetic studies with larger number of data points.
3) The present results of batch experiments can be compared with column experiments varying the flow rate of solution.
4) In overburden material, besides goethite clay minerals, amorphous hydrated iron oxides and organic materials can be present. So the role of these constituents of the soil in anion adsorption can be studied.

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